FACTORS INFLUENCING THE ISOTOPICALLY EXCHANGEABLE PHOSPHATE IN SOILS

PART II. THE EFFECT OF BASE SATURATION WITH SODIUM AND CALCIUM IN NON-CALCAREOUS SOILS

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The retention of phosphate ions by soils and soil-clay minerals has been related to the valency of the saturating cation (Aderikin ¹ Allison ², Barbier *et al.* ⁴, Pratt and Thorne ⁸, Wild ¹⁰). Increased retention is invariably observed as the valency of saturating cation increases; this increase is considerably accentuated as the pH of the soil suspension is raised above 6 to 7. A cationic series has been suggested (Aderikin ¹) in the order of decreasing P-retention

The phosphate-ion activity in solution in equilibrium with these cation-saturated materials also depends on the activity and the valency of the cation in the solution; this may play a considerable part in the observed retention of phosphate by soils and allied materials.

The retention of phosphate by the soil and the phosphate concentration in the equilibrium soil solution are related to the 'labile phosphate' of the soil. Klechkovskii and Zherdetskaya ⁷ found that phosphate sorbed on potassium- and calcium-saturated forms of chernozem, peat podzol, and krasnozem soils was equally exchangeable isotopically. Little detailed work on this topic has been published. The present work examines the influence of ex-

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changeable cations on the labile phosphate by applying methods used in earlier work (Talibudeen⁹, Arambarri and Talibudeen³)

METHODS AND MATERIALS

TABLE 1

Description of soils					
Soil	pH in 0.02 M KCl	Total P, mg P %	Clay %	Location	Brief description
A	6.8	90.6	20	Rothamsted	Highfield
B	6.9	113.0	19	Rothamsted	Broadbalk Section V (8) unlimed
C	6.8	136.5	20	Rothamsted	Park Grass Plot 4 (i) limed
D	6.8	56.7	20	Rothamsted	Park Grass Plot 2 (i) limed
E	6.0	62.5	11	Old Kennington	Superphosphate-treated plot
F	6.8	119.0	10	Shardlow	Plot F 11. (Blood ⁶)
G	6.9	20.8	15	Seville, Spain	Unmanured terra rossa

Preparation of cation-saturated soils

The soils were treated repeatedly with molar solutions of NaCl and CaCl₂ adjusted to pH 6.8–7.0, and washed with alcohol and acetone until all chloride ions were removed. The samples were air-dried. A calcium-saturated sample of soil A using 0.01 molar calcium chloride was also prepared; analyses of the decantate showed that complete calcium saturation of 10 g soil was achieved with four 80 ml volumes of the calcium chloride solution.

Experiment 1

The total isotopic exchange was determined at isotopic equilibrium in Na- and Ca-saturated samples of soils B to G in 0.02 M NaCl and 0.0067 M CaCl₂ respectively; the total labile phosphate was calculated from the equilibrium phosphate concentration in solution and the fraction of P³² left in solution at equilibrium. Although no difficulty was experienced in separating the soil from the solution by centrifugation at high speeds, the solutions from the Na-soil experiments (0.02 M NaCl) mostly had a faint, brownish yellow tinge which could be attributed to the partial peptisation of the fine fraction in the soil. This would not affect the P³²-content of the solutions determined by counting but may give a positive error in their total phosphorus contents by the molybdenum-blue method.

For comparison, labile-phosphate values were also similarly determined in untreated samples of soils A to G suspended in 0.02 M KCl.

Experiment 2

Using methods described earlier (Arambarri and Talibudeen³) the isotopic exchange of orthophosphate ions in Na- and Ca-saturated samples of

soil A in equilibrium with 0.02 *M* NaCl and 0.0067 *M* CaCl₂ respectively, was determined at 25° and 35° C.

RESULTS AND DISCUSSION

EXPERIMENT 1

Klechkovskii and Zherdetshaya⁷ showed that phosphate ions fixed on calcium and potassium saturated soils are equally capable of isotopic exchange. Table 2 gives the distribution of the

TABLE 2

The labile phosphate in mg P per 100 g soil in sodium- and calcium-saturated soils * and its partition between the soil and the solution at 22–25° C and a dilution of 1 : 200 **						
Soil	Na-soil in 0.02 <i>M</i> NaCl		Ca-soil in 0.0067 <i>M</i> CaCl ₂		Untreated soil in 0.02 <i>M</i> KCl	
	P in solution	Total labile <i>P_e</i>	P in solution	Total labile <i>P_e</i>	P in solution	Total labile <i>P_e</i>
A	3.1	13.3	0.62	11.1	0.8	11.3
B	17.3	33.5	3.0	24.7	8.7	30.5
C	22.6	35.7	6.6	31.7	20.0	44.2
D	0.6	5.3	0.1	6.6	0.3	4.3
E	8.1	12.8	2.1	11.8	6.7	13.7
F	17.0	30.7	2.5	20.6	9.2	27.2
G	0.9	2.0	0.1	1.6	0.6	1.7

* Saturated by washing with molar solutions of sodium and calcium chlorides as described in "Methods".

** These exchanges were carried out in solutions of equal ionic strength $\mu = 0.02$ at a dilution of 0.5 g soil in 100 ml solution.

total labile phosphate P_e into the phosphate in solution P_{ss} and on the soil surface P_s for soils A to G. Results are given separately for the sodium- and calcium-saturated soils and for the untreated soils. The labile phosphate in six of the seven sodium-saturated soils is higher than in their calcium-saturated forms. This may be attributed partly to the contamination of the isotopically exchangeable phosphate in the solution in equilibrium with sodium-saturated soils by non-exchangeable (partly organic) forms of phosphate. If the constancy of the product of the concentrations of cations and $H_2PO_4^-$ ions can be taken as a guide to the relative magnitudes of

the concentrations of orthophosphate ions in the NaCl and CaCl₂ solutions

$$i.e. (M)^{\frac{1}{v}} \cdot (H_2PO_4) = \text{constant}$$

where v is the valency of the cation M ,

the 'true' orthophosphate concentration in the NaCl solutions can be calculated using that in the CaCl₂ system as a reference. Using the observed partition coefficient of radioactivity in the Na-system, its 'true' labile phosphate can now be calculated and compared with the values for the Ca-systems. The results of these computations are given in Table 3, which shows that for soils B and F

TABLE 3

Comparison of calculated and observed [H ₂ PO ₄] concentrations and labile-phosphate values in sodium soils with values in calcium-saturated soils						
Soil	[H ₂ PO ₄] concentrations * in molarity $\times 10^7$			Labile-phosphate values (P_t) in mg per 100 g soil		
	NaCl Solution		CaCl ₂ solution	Na-system		Ca-system
	Observed	Calculated		Observed	Calculated	
A	31.3	25.4	6.2	13.3	10.8	11.1
B	173.0	123.0	30.1	33.5	23.8	24.7
C	227.0	271.0	66.2	35.7	42.7	31.7
D	6.4	4.7	1.1	5.3	3.9	6.6
E	80.9	87.5	21.4	12.8	13.8	11.8
F	171.0	103.0	25.2	30.7	18.6	20.6
G	8.2	4.1	1.1	2.0	1.0	1.6

* Using a pK'' value of 7.016 at 25° C for phosphoric acid at $\mu = 0.02$ (Bjerrum⁵).

where a marked difference is observed between the values for sodium and calcium systems, the calculated values for the sodium systems are similar to the observed values for the calcium system. In soil C, however, the [H₂PO₄] concentration observed in solution is much lower than the calculated value, suggesting the presence of a multivalent cation *e.g.* [Al(OH)]⁺⁺ or [Fe(OH)]⁺⁺ in the NaCl extract. Expressing the distribution of phosphate between the observed phosphate in solution and in the soil by a partition ratio:

$$\frac{\text{P in solution}}{\text{Labile P in soil}}$$

gives a ratio in the sodium systems 5 to 9 times higher than in calcium systems. Thus it appears that the total labile phosphate computed from isotopic-exchange experiments is not sensitive to

the valency of the saturating cation provided appropriate correction can be made for non-isotopically exchangeable forms of phosphate in the solution.

Influence of pre-treatment for base-exchange saturation

These soils were also examined without pretreatment with saturating solutions. A comparison of the isotopic exchange data in the treated and untreated soils is of considerable interest (Table 2). The untreated soils were suspended in 0.02 *M* KCl to determine the labile phosphate, the number of K-ions in solution thus being considerably greater than the exchangeable cations in the soil. Even if the exchangeable cations were predominantly divalent, a fair degree of cation exchange is to be expected with the formation of a mixed ($\text{Na}^+ + \text{K}^+ + \text{M}^{++}$) soil containing an increased percentage of exchangeable, monovalent potassium ions, the properties of this system being intermediate between those of the Na- and Ca-systems. A comparison of the data show that this is realised in the magnitudes of the phosphate in solution; in fact, the phosphate concentration of the solution in equilibrium with the untreated soil indicates the valency of the predominating exchangeable cation in the soil. For instance a comparison of soils D and G shows that their P-concentrations in the Na- and Ca-systems are very similar. The P-concentration for the untreated soil is more than double that of soil D suggesting that the predominating, exchangeable cations in the two untreated soils are monovalent and divalent respectively.

Generally the labile phosphate in the untreated soils and the Na- and Ca-saturated soils are of the same order even when no corrections are made for the non-isotopically exchangeable phosphate in solution.

In the following section the influence of the valency of the cation, of temperature, and of the concentration of the saturating solution of calcium chloride on the distribution of the components of the labile phosphate and their rates of isotopic exchange in soil A are examined using methods described earlier (Arambarri and Talibudeen ³). The labile phosphate P_s in the soil can be divided into three or four fractions P_0 , P_1 , P_2 and P_3 according to the speed with which they can exchange phosphate ions isotopically with the phosphate in solution P_{ss} .

EXPERIMENT 2

Valency of saturating cation

The labile phosphate P_s left in the soil after the extraction of phosphate by the equilibrium solution increases in going from sodium to calcium saturation due to the decrease in the phosphate in solution P_{ss} (Table 4). The rates of exchange for the 'rapid'

TABLE 4

The distribution of the labile phosphate P_e into its components in sodium and calcium forms of soil A and the effect of temperature on this distribution								
Units: <i>Amounts</i> mg P per 100 g soil;								
Rate of isotopic exchange in mg P per 100 g soil per hour								
Components	Sodium-saturated Soil				Calcium-saturated Soil			
	25° C		35° C		25° C		35° C	
	Amount	Rate	Amount	Rate	Amount	Rate	Amount	Rate
'Rapid', P_1	2.2	Fast	2.1	Fast	2.9	Fast	4.3	Fast
'Medium', P_2	1.4	0.22	1.5	0.38	0.3	0.05	0.3	0.05
'Slow', P_3	6.6	0.04	10.4	0.079	7.4	0.01	12.6	0.008
Total in Soil, P_s	10.2	—	14.0	—	10.5	—	17.2	—
'Solution', P_{ss}	3.1	—	3.4	—	0.6	—	0.6	—
Total in system, P_e	13.3	—	17.3	—	11.1	—	17.8	—

fraction are not changed significantly at 25° or 35° C by Na- and Ca-saturation, but the rates for the medium and slow fractions are between 4 and 10 times greater at 25° and 35° C respectively, in the Na-system. This suggests that there is an intimate linkage between the exchangeable calcium ions and phosphate ions in the 'medium' and 'slow' components, and that the 'rapid' component is relatively insensitive to the exchangeable cation. The 'medium' and 'slow' components together constitute from 73 to 85 per cent of the labile phosphate left in the soil, thus this behaviour seems to support the hypothesis of a calcium-phosphate complex being formed in the surface-adsorbed phosphate in which the exchangeable calcium ions play an important role.

Influence of temperature

Table 4 shows that the total labile phosphate in the Na- and Ca-systems increases appreciably with a 10° C rise in temperature, but whereas the phosphate in solution increases by about 1 per cent per °C in the Na-system, there is no significant change in the phosphate

concentration of the solution in the Ca-system with temperature. The increase in the labile phosphate at 35° C shows clearly in the 'slow' phosphate, although in the Ca-soil there is also a small increase in the 'rapid' fraction. The difference in the total labile phosphate between the two systems at 25° C is removed by increasing the temperature to 35° C.

It was shown earlier that substituting sodium ions for calcium ions in base-exchange positions did not affect the rate of the 'rapid' exchange but increased the rates of the 'medium' and 'slow' exchanges. The influence of temperature also suggests a change in the nature of the linkage between the exchangeable cations and adsorbed phosphate in going from Ca^{++} to Na^+ ions. Here again, there is no significant change in the rate of the 'rapid' exchange in the Na- or Ca-systems, but whereas in the Na-systems the rates of 'medium' and 'slow' exchanges are doubled with a 10° C rise in temperature the corresponding values in the Ca-system are unaltered. This behaviour strongly supports the conclusion arrived at in the previous section that the exchangeable calcium ions are more strongly linked than sodium ions with the 'medium' and 'slow' exchanging phosphate ions and that the linkage is not temperature-sensitive in the range 25° to 35° C.

Influence of the concentration of CaCl_2 solution used for base saturation of the soil

As exchangeable calcium ions affected the magnitude and the behaviour of the 'medium' and 'slow' components of the labile phosphate, it was thought necessary to investigate whether this was due to the precipitation of a calcium-phosphate compound on the surface of the soil during the procedure used for base saturation with molar calcium chloride. From the known solubility products of calcium phosphates (Bjerrum ⁵), a simple calculation shows that a 0.01 *M* CaCl_2 could not precipitate any of these compounds in these soils. Table 5 shows the isotopic exchange for soil A, saturated with calcium ions by 0.01 *M* and 1.0 *M* CaCl_2 solutions. These results clearly demonstrate that the 'medium' and 'slow' components are unaffected by the concentration of the saturating solution either in magnitude or in the rate at which they exchange. This emphasises the fact that the differences observed between the rates of exchange and between the phosphate exchanging

TABLE 5

The labile phosphate and its components at 25° C in the calcium-saturated form of soil A in equilibrium with 0.0067 <i>M</i> CaCl ₂ Units: <i>Amounts</i> mg P per 100 g soil; <i>Rate</i> of isotopic exchange in mg P per 100 g soil per hour				
Components	Base saturation with 0.01 <i>M</i> CaCl ₂		Base saturation with 1.0 <i>M</i> CaCl ₂	
	Amounts	Rate	Amounts	Rate
'Rapid' <i>P</i> ₁	4.3	Fast	2.9	Fast
'Medium' <i>P</i> ₂	0.3	0.04	0.3	0.05
'Slow' <i>P</i> ₃	8.3	0.009	7.4	0.01
Total in Soil <i>P</i> _s	12.9	—	10.5	—
Solution <i>P</i> _{ss}	0.4	—	0.6	—
Total in System <i>P</i> _e	13.3	—	11.1	—

isotopically in sodium- and calcium-saturated soils can not be caused by precipitated calcium phosphates in the latter.

Wild¹⁰ showed that in an aluminium-saturated resin, foreign cations added to the system influence the reaction between added phosphate and the aluminium according to their valency and the size of their hydrated forms. He suggests that the retention of phosphate by clays due to this reaction differs only in degree from that of the resin; he advances two alternative explanations for this behaviour namely that the exchangeable cations influence (*i*) the distribution of phosphate ions within the diffuse part of the electrical double layer associated with the resin or clay and (*ii*) the amount of reactive aluminium released from the resin or clay. Although the evidence given by Wild for the role of reactive aluminium is not entirely conclusive, it plausibly explains the decreased mobility of the more slowly exchanging forms of phosphate in calcium-saturated clays. Base saturation of the clay with a cation of higher valency would increase the activities of free aluminium and phosphate ions and bind the adsorbed phosphate more strongly due to increased interaction between the two ions. The degree of reversibility of such an interaction may be partly responsible for the anomalous behaviour of the soil phosphate *e.g.* the changes observed in the equilibrium phosphate concentrations in the soil solution after the consecutive "wetting" and "drying" of the soil.

SUMMARY

The effect of base saturation of non-calcareous soils with sodium and calcium on their total labile phosphate was studied in solutions of sodium

and calcium chlorides of the same ionic strength ($\mu = 0.02$). The total labile phosphate in 6 out of 7 soils was between 8 to 40 per cent higher in sodium-saturated soils than in calcium-saturated soils. A much larger part of the total labile phosphate was found in solution in the sodium-saturated soils. The ratio of phosphate in solution in these soils to that in calcium-saturated soils varied from 3.4 to 8.1 with a mean value of about 5.5 as compared with a theoretical value of 4.1. A method is suggested for obtaining 'corrected' values for the abnormally high phosphate concentrations in solution from sodium-saturated soils. 'Corrected' values give smaller differences between the total labile phosphate in sodium and calcium forms of these soils.

Rates of isotopic exchange of the more slowly exchanging forms of soil phosphate were measured at 25° and 35° C for the sodium- and calcium-saturated forms of one Rothamsted soil. At 25° C these rates were four times higher in the sodium-saturated soil than in the calcium-saturated soil although the total labile phosphate in the two forms was the same. Increasing the temperature to 35° C doubled these rates of exchange in the sodium-saturated soil but had no effect on the calcium-saturated soil. This suggests that the cation-exchangeable calcium is strongly linked to the slowly-exchanging forms of phosphate in the soil.

No differences were observed in the rates of isotopic exchange of phosphate in this soil after calcium saturation with either 0.01 molar or 1.0 molar calcium chloride. The precipitation of calcium phosphates during the calcium-saturation procedure could not therefore be responsible for the observed differences between sodium- and calcium-saturated samples.

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